Advanced Ablative composites for Aerospace applications

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Abstract- The external surface of a re-entry space vehicle experiences high heat flux and temperatures of the order of 2500°C during re-entry into the atmosphere and the internal contour of a rocket motor nozzle has to encounter temperatures above 2000°C during its operation. Special Thermal Protection Systems (TPS) are employed to protect the rocket hardware and re-entry capsule from such extreme thermal environments. Ablative composites are cost-effective and well-proven candidates for such applications. However, processing, characterisation and qualification of ablatives are quite complex and involves long cycle times.

Ablation is a heat and mass transfer process in which a large amount of heat is dissipated in a very short period of time with sacrificial loss of material. Ablative composites are polymeric composites where the reinforcement is generally a fibre with high melting point like Carbon or Silica and the matrix is a high char yielding resin like phenolics. In this paper, the process of ablation, the physical and chemical changes and the process of synthesis of ablatives are clearly elaborated. The recent advances in design, development, characterisation and testing of carbon and silica phenolics are explained with examples.

The process sequence and customised equipments used for the synthesis and characterisation are described. The raw materials, critical process parameters, quality control mechanisms, non-destructive testing methods etc are covered. The defects which were observed during the realisation and the corrective measures taken to solve them are explained.

Different laminate and subscale level tests have been done to qualify the process and verify the design margins. Finally a full scale rocket engine test is carried out for qualification before induction into an operational launch vehicle.

Keywords: *ablatives, composites, carbon, silica, phenolics, hydroclave, curing, tape-winding, moulding, rocket nozzles.*

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1. Introduction

Ablative composites are an elite class of composites made of high melting point fibers and polymeric resins with very high char yield. Commonly used reinforcements include carbon, graphite, silica, glass, asbestos etc and resins include phenolics and furfuryl alcohol. An ideal ablative composite should possess high heat of ablation, high enthalpy of phase change, sufficient strength, high specific heat, high thermal shock resistance etc. At the same time, it should have low thermal conductivity, medium density, low molecular weight for the volatiles evolved during pyrolysis and as low an erosion rate as possible.

Ablation is an orderly heat and mass transfer process in which a large quantity of heat energy is dissipated in a very short period of time by sacrificial loss of material at a rate which can be estimated. It is a very complex process including many physical and chemical transformations including phase changes like melting, vapourisation, sublimation and pyrolysis. Many endothermic reactions occur during the process.

The ablative composites encounter extremely hostile conditions during the motor operation. The high temperature, pressure, velocity of hot exhaust gases, heat flux, particle impingement of the solid propellant particles etc contribute to harsh environment inside the nozzle. High temperature resistant metals or alloys alone cannot survive the operating conditions in a solid rocket motor. While the metallic structure provides the necessary structural capability, high performance composite materials are required for thermal protection. Ablative composites generally use Carbon or Silica as the reinforcement and phenolic resin as the matrix resin.

When the ablative is subjected to a very high heat flux as the hot exhaust gases pass through the nozzle, the surface temperature increases rapidly. Due to the low thermal conductivity of the material, the temperature builds up on the surface rather than the heat getting conducted to the backup structure. As the temperature near the surface reaches the pyrolysis temperature of the resin in the composite, decomposition of resin takes place. This leads to the formation of char on the surface of the ablative. As time progresses, the extent of char increases or the char front advances into the thickness of the material. Then the surface material starts eroding; erosion of the material can be due to the thermal degradation of the material and/or due to the mechanical erosion caused by metallic particle impingement due to the Aluminium particles of the solid propellant flowing along with the hot exhaust gases. As the layer on the surface erodes, the next layer gets exposed

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and the process continues.

During pyrolysis, the volatile gases evolving at the reaction zone finds its way through the charred zone taking away significant amount of heat. Similarly, melting of the resin as well as the fibers also consume some heat. With all these processes, a large quantity of heat is expended with sacrificial loss of material, thereby, protecting the metallic substrate from thermal degradation.

As the ablative composite is exposed to heat, it acts as a heat sink and its temperature starts rising. At the pyrolysis temperature, the decomposition of the composite starts, evolving gases, leaving the rigid porous carbonaceous substance called passive char. During the further advancement of the heating zone, the pyrolysis gases developed, absorb the heat from the passive char layer and dissociate itself into solid substrates which fill the porous char and builds pressure in the porous cavities. As the pressure exceeds a threshold limit, char spallation takes place. All the above reactions are of endothermic in nature.

2. Experimental Details

Ablative composites were synthesised from phenolic resin as matrix and carbon/silica fibres. Phenolic resin is synthesised from phenol and formaldehyde. The typical properties of the resin matrix are given below:

TABLE I : PHENOLIC RESIN PROPERTIES

Sl. No	**Important properties**	
	Parameters	**Typical values**
1	Specific gravity at 30°C	1.2
2	Solid content, %	63.5
3	Viscosity at 30°C, cps	250-300
4	Degree of advancement, ml	13.5
5	Free phenol content, %	5
6	Free formalin content, %	2

Carbon/Silica fibers are used as the reinforcement. Rayon based Carbon fiber is preferred for ablative applications as it provides lower thermal conductivity and higher interlaminar Shear strength because of crenulated cross-section. Carbon fabric is made by weaving Carbon fibres with carbon content greater than 94%. This is made by successive carbonization of rayon. Polyacrylonitrile (PAN) and Pitch based carbon fabrics can also be used. 8 Harness Satin weave was chosen as the weave pattern considering the drapability for ease of processing. Typical parameter values of the carbon fabric used is listed below:

TABLE II: IMPORTANT PARAMETERS OF CARBON FIBERS

Sl. No	**Important properties**	
	Parameters	**Typical values**
1	Carbon content, %	94-96
2	Sodium content, ppm	600
3	Ash content, %	0.20
4	pH	8
5	Breaking strength, kg/inch width	80-100
6	Areal density, gm/sq.m	250-300
7	Thickness, mm	0.3-0.4
8	Specific gravity	1.75
9	Thread count, ends/inch	45-55

The carbon/silica fabric is impregnated with phenolic resin in an impregnation plant which can be either vertical or horizontal. The block schematic of a typical impregnation plant is given in figure 1.

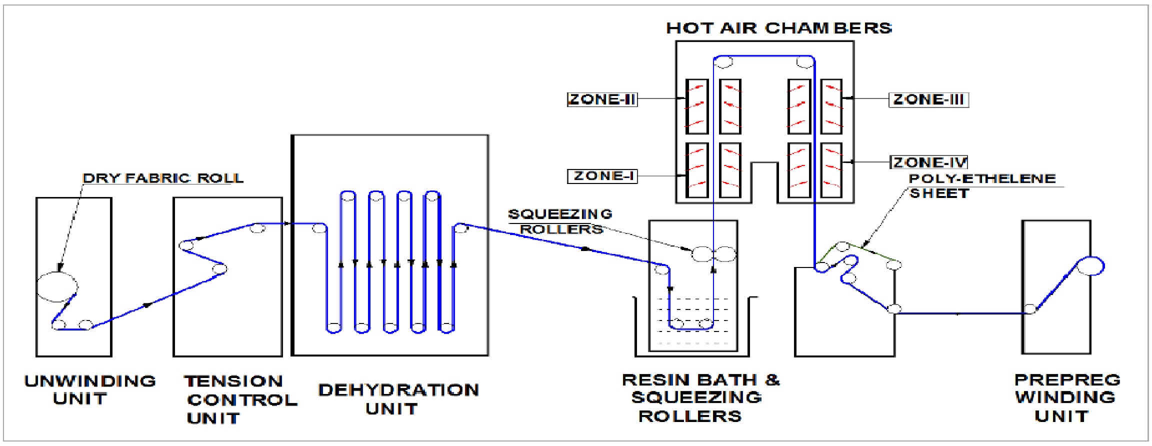


FIGURE 1: **BLOCK DIAGRAM OF AN IMPREGNATION PLANT**

Initially, the fabric is dehydrated above 100°C to drive out the moisture. Then it is passed through a resin tank to absorb the resin. The tension in the fabric is to be closely controlled to ensure uniform wetting. The squeeze rollers can be adjusted to control the resin content in the prepreg. It is then passed through heating zones to advance the resin. The resultant material is called Carbon/Silica phenolic prepreg. The important parameters of the prepreg are,

TABLE III: IMPORTANT PARAMETERS OF CARBON PHENOLIC PREPREG

Sl. No	Important properties	
	Parameters	**Achieved values**
1	Volatile content, (%)	4-10
2	Dry Resin content, (%)	35-40
3	Wet Resin content, (%)	40-50
4	Degree of advancement, Chang's index, (ml of water)	22-28

The prepreg is cut into the form of plies using a template and are either stacked together or wound on a metallic mandrel. The prepreg layup is compacted either giving vacuum or in a hydraulic press to get good as-wrapped density.

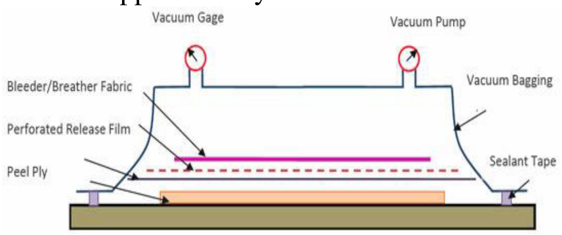


FIG. 2: SCHEMATIC OF LAYUP OF PREPREG

Fig.2 shows a schematic of the layup with bleeder/breather film, perforated release film and the vacuum bag in position. Perforated release film serves dual purpose; perforations allow the excess resin and volatiles to freely flow out of the liner and the release film prevents the unwanted adhesion of the liner to the mould. The bleeder material shall absorb the excess resin squeezed out of the liner. The vacuum bag is made from special grade polymer films capable of withstanding the curing temperature and pressure. For curing in Hydroclaves, impermeable high temperature resistant rubber bags with about 600% elongation are used. Alternatively, the prepreg is wound onto a metallic mandrel under pressure from a Teflon-coated metallic roller. The prepreg is preheated using a hot air blower and cooled using liquid nitrogen to ensure adequate flow of resin. This operation is done on a customised center-lathe modified with provisions for prepreg heating, cooling, very accurate pitch control, tension control devices, tape alignment systems and features to tilt the bed to accommodate winding mandrels of different angles and sizes.

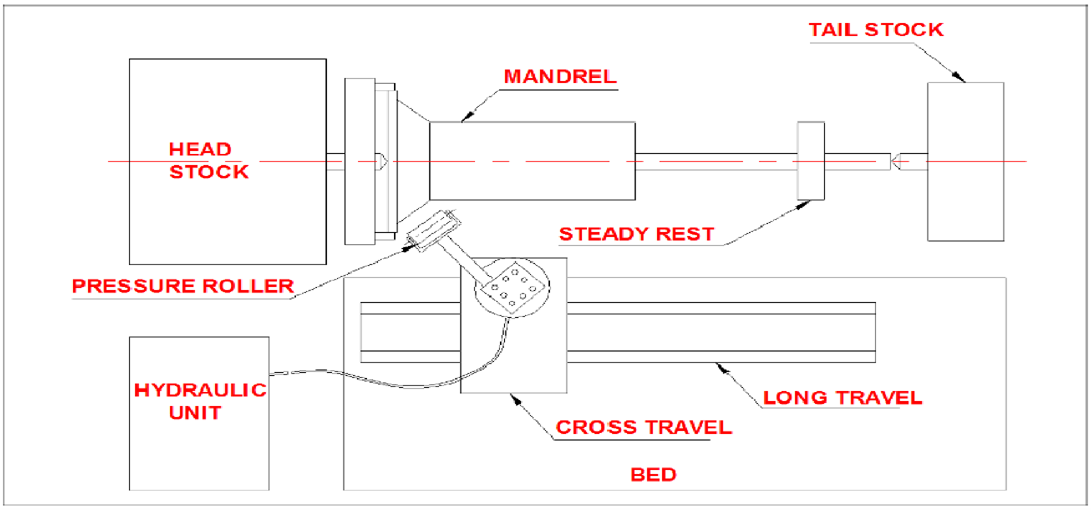
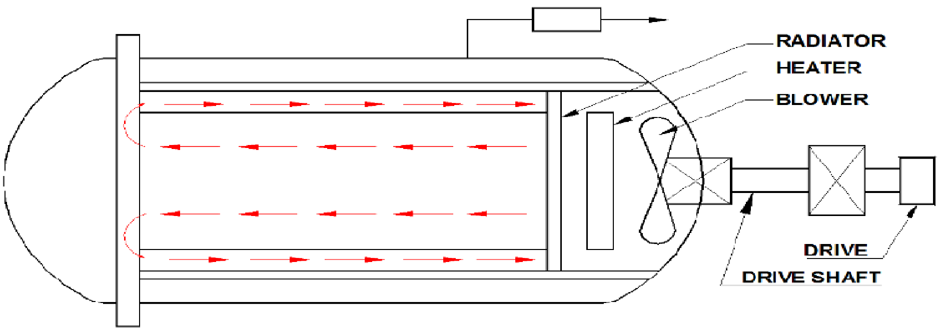


FIGURE 3: TAPE WINDING MACHINE

Curing or polymerisation is the most critical operation in the processing sequence of an ablative composite. It is done in sophisticated equipment like a hydroclave or autoclave under high temperature and pressure. After layup, the ablative liner is put in a vacuum bag and cured at 150°C under pressure of 40 to 60 bar. Cross-linking of molecules of the polymer or polymerisation is achieved by curing under high temperature and pressure. In an oven, only heating is possible, whereas in an Autoclave/Hydroclave pressurisation is also done. The pressurising medium is air in an Autoclave which can go upto 10 bar pressure, while in a Hydroclave, pressure upto 70 bar can be applied since water is the pressurisation medium.



AUTOCLAVE

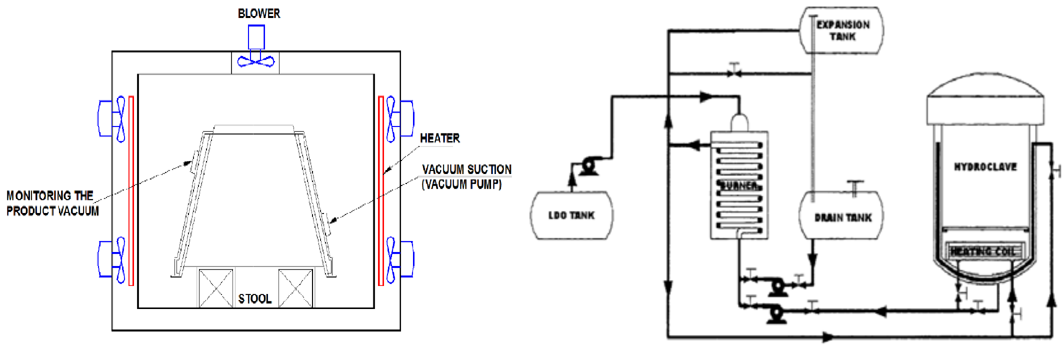


FIGURE 4: OVEN, AUTOCLAVE & HYDROCLAVE

The product with the vacuum connections is leak tested to ensure a minimum vacuum level. The product further undergoes a series of cure steps in a phased manner such as heating, pressurization, soaking, depressurization and cooling in the Hydroclave to get a defect free cured product. The heating rate, pressurization steps, maximum compaction pressure, cooling rate and the depressurization sequence are to be selected, considering the density of the final product, type and quantity of prepreg, tool design and previous experience of curing similar quality products. The product temperature at identified locations is monitored as the product temperature gradient during the entire curing cycle is to be minimized to avoid thermal stresses and to achieve the desired thermal and mechanical properties.

As the phenolic resin undergoes condensation polymerization reactions during the heating and soaking phase, the volatile compounds evolved such as alcohol, water vapour, free phenol etc. are to be completely sucked and positively driven out by giving sufficient compaction pressure and vacuum. Insufficient pressure and inadequate vacuum for curing will lead to delaminations and defects in the cured product. The pressurization is done based on the product temperature and maximum pressure is applied at a specified product temperature at which the resin changes from the visco-elastic to the viscous stage. When the phenolic resin is heated, viscosity of the resin decreases initially as the temperature rises, reaches a minimum value and then starts rising on further heating. If the maximum pressure is applied at low viscosity then more resin will be squeezed out resulting in insufficient resin and delaminations in the cured product, and on the other hand if the pressure is applied at a high viscosity, the compaction pressure will not get transmitted to the inner regions of the product. The importance of pressure application based on the product temperature is to apply the maximum pressure at a reasonable viscosity level to avoid excess resin squeeze out as well as to enable uniform compaction by transmitting

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the pressure as a viscous medium rather than at a solidified state which does not permit the matrix penetration between the reinforcement. Another peculiar phenomenon in the curing of the ablative composites is the "resin exotherm phase". During the initial phase of heating, it is quite normal that the product temperature will always be lagging the water temperature in the Hydroclave. However at a particular stage the product temperature especially in the middle regions starts rising fast and goes above the vessel water temperature. Even if the vessel temperature is not increased, the product temperature rises continuously superseding the vessel temperature due to a phenomenon peculiar to the phenolic resins. At this juncture the vessel temperature also needs to be brought along with the rise in temperature of the product to minimize the product temperature gradient. The maximum pressure is applied during the exotherm phase. The exotherm regime and the pressure application at the required product temperature are unique and very important to achieve defect free and quality products with better properties. A typical cure cycle is given below.

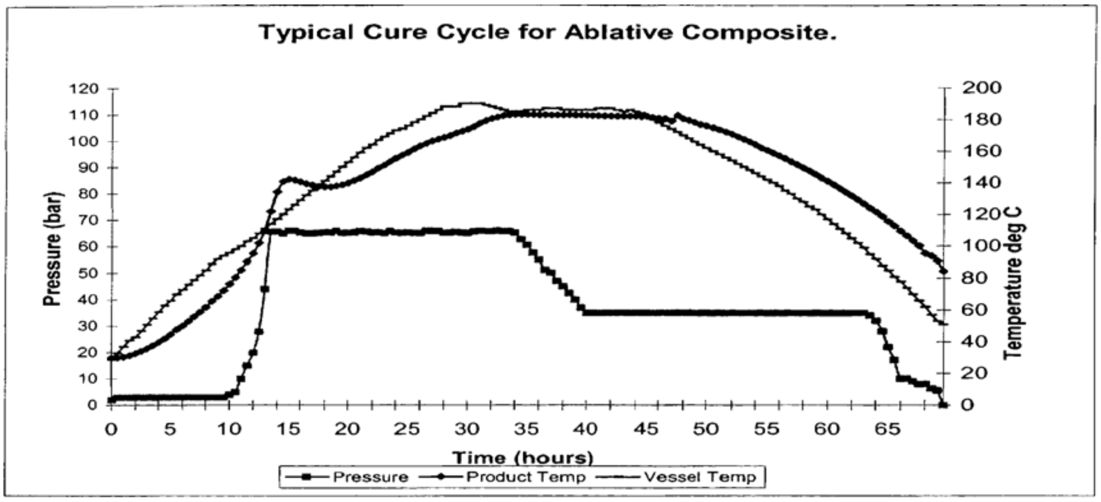

FIGURE 5: A TYPICAL CURE CYCLE FOR ABLATIVES

The product is further heated to the specified temperature (keeping the maximum pressure) and soaked at this temperature to complete the polymerization reactions. After soaking, the product is slowly cooled to the room temperature keeping the product temperature gradients to a reasonable minimum value to avoid thermal stresses, which are critical in the cooling regime. Parallelly, pressure is also reduced in a phased manner and is totally released as the product reaches a temperature less than 90°C. Thereafter product is allowed to cool naturally to room temperature before extraction from the tool.

The vacuum pumps are connected to the vacuum ports of the hydroclave vessel through valves and resin traps. The vacuum bagged product is connected to the vacuum ports in the vessel through flexible SS vacuum hoses. The volatile compounds formed during the curing and the excess resin is sucked by the vacuum pump and the volatiIes are periodically removed from the resin trap. Vacuum bagging is very important since any bag failure or vacuum leak will lead to water seepage and can result in product delaminations.

Hydroclaves use thermic fluid heating system. The light diesel oil (LDO) stored in the LDO tank is pumped, injected and fired in the burner to heat the thermic fluid which is circulated from the burner to the hydroclave through piping. The hot thermic fluid heats the water in the hydroclave through heating coils and jacketed vessel areas of the hydroclave. The thermic fluid heating system enables a controlled heating for the composite product. The thermic fluid circulation pump has to withstand the high temperatures of the order of 200°C and shall work continuously for about 70 percent of the cure cycle duration. The capacity of the burner system depends on the vessel volume and the maximum heating rate required. Positive displacement plunger pumps and control valves enable pressurization and depressurization. The pressure inside the pressure vessel needs to be positively maintained above the critical pressure of water at that temperature to avoid steam formation and associated safety problems. The pressure relief valves set above the maximum operating pressure relieve excess pressure in case of overshoot. High rate of pressurization is possible in hydroclave and this helps in immediate pressure rise required during the exotherm phase. The pressure vessel, rubber gasket, control valves and the pressure pipe joints in the pressurization and depressurization lines are very critical as any leak in any of these lines is not permissible from the safety point of view as the pressure drop to below the critical pressure value forms steam. If the joints are perfect and there is no leak, the load on the pressure pump will be so less that during the heating phase the requirements of switching on the pump is rare, as the increase in temperature itself will be sufficient to provide the required pressure increment. For redundancy in the pressurization two pressure pumps are provided in the system.

The water temperature inside the pressure vessel needs to be maintained uniform to enable uniform heating of the product. The water circulation system maintains the spatial distribution of temperature within reasonable limits. A high capacity water circulation pump circulates water in the vessel at all the working pressures and temperatures. Interlocks are made in such a way that pressurization is possible only after switching the

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circulation ON. The circulation pump is rugged and highly reliable, as it has to work continuously for the entire cure cycle.

The cooling medium is water, circulated through cooling coils housed inside the pressure vessel. Since the cooling starts at high temperatures of the order of 150°C and above depending on the type of phenolic resin system, water entering the cooling coils immediately attains 150°C causing sudden steam formation resulting in very high back pressure and knocking in the cooling pipes. It is very important to note that cooling water circulation needs to be at extremely low and controlled flow rate to minimize the pressure drop due to sudden temperature fall inside the Hydroclave. Special control valves having very low to medium and high flow rate are essential for controlled cooling without pressure drop.

Rust preventive coating / painting over the interior surface of the Hydroclave is a mandatory requirement as the rusting will reduce the effective wall thickness and thereby decreasing the available margin.

After curing, the ablative composite is machined to the required configuration using special tools. Polycrystalline diamond (PCD) or Tungsten Carbide tools are used due to the abrasive nature of the material. Machining of ablatives is totally different from conventional materials like metals; here the material removal is in the form of carbon or silica powder and not in the form of chips. This necessitates dust collection suction systems at the cutting location which has to move along with the tool post. Coolant is not used during the machining of ablatives as it would cause deterioration in the properties of the composite.

3. Results and Discussion

Dimensions of the required part are measured and Non-destructive testing is done to confirm that no defects were present in the liner. Common defects likely in ablative composites include delaminations, cracks, voids, porosity, resin lean lines, resin rich lines, resin starvation, resin patches, non-uniform resin distribution, waviness, wrinkles etc. Visual inspection, tap test and alcohol wipe test was done initially. This was followed by Ultrasonic inspection by Pulse echo and through transmission methods. Wherever the signal strength was less or suspected delaminations were reported, tangential radiography was done to rule out the presence of delaminations.

Co-cured specimens are tested for mechanical and thermal properties. Specimens are fabricated from the end rings of the liners as per ASTM standards and tested.

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4. Conclusion

The indigenous manufacturing processes for the development of high performance thermal protection ablative composites have been discussed in detail. The experimental details of synthesis and processing of carbon phenolic ablative composites are explained. The processed ablatives were characterized and all the critical properties have been evaluated. The various state-of-the art process equipments for ablative composite manufacturing have been explained. Indigenous process developments and equipment design has been discussed. These ablative composites are being used in the launch vehicles satisfactorily.

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References:

1. M. Balasubramaniam, *Composite materials and Processing,* CRC Press, USA. **(2013)**.
2. Fitzer, E; Manocha, L M *Carbon reinforcements and Carbon/Carbon components***,** Springer Verlag, Berh **(1998)**.
3. Sutton, K., *An Experimental study of a Carbon-phenolic ablation material*, NASA Technical Note NASA-TN-D 5930. (**1970**)
4. T.L.Elegange and R.R. Bowman, *Nozzle fabrication for space shuttle solid rocket motor,* AIAA/SAE 14th Joint Propulsion Conference.
5. H.R. Clements and G.T. Ward, *Development of fabrication techniques for large solid booster nozzles*, AIAA 6th Solid Propellant Rocket Conference, Washington DC.
6. Mohan Kumar. L, Nikhil K Mawari, et al, *Development of Bias wrapping technology for Ablative liners in S139 Solid rocket motor,* INCCOM13 Proceedings, November 2014.
7. Gutowski Timothy G, *Advanced Composite Manufacturing*, Wiley, 1997.